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Spectral Equations-Of-State Theory for Dense, Partially Ionized Matter

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May 18, 2004

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The Schroedinger equation is solved in time and space to implement a finite-temperature equation-of-state theory for dense, partially ionized matter. The time-dependent calculation generates a spectrum of quantum states. Eigenfunctions are calculated from a knowledge of the spectrum and used to calculate the electronic pressure and energy. Results are given for LiD and compared with results from the INFERNO model.

I. Introduction

There has been much interest recently in improving the accuracy of equations-of-state databases for dense, partially ionized materials [1]. In particular quantum self-consistent-field (QSCF) models [1-3] are replacing the older Thomas-Fermi-Dirac (TFD) model [4-5], and in the future condensed-matter models (known as warm dense matter models [6]) may replace the QSCF models.

The QSCF models [1-3] suffer from difficulties in converging the self-consistent fields and in uncertainty in boundary conditions at the ion-sphere radius. The latter problem is especially troubling because it leads to author-dependent results based on how a given author may decide to satisfy the theorem of wave function continuity at boundaries and at the same time mimic condensed matter effects which more powerful theories [6] treat explicitly. In contrast an advantage of the TFD model [4-5] and of a recenly presented quantum-shell corrected TFD model [7] is its use of unambiguous boundary conditions.

In this paper we present a quantum theory which improves on the problems of convergence and boundary-condition uncertainty. Our

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theory also takes advantage of recent advances in computational algorithm development [8-10] for solving the Schroedinger equation as a parabolic partial differential equation in the time and three spatial dimensions. This enables the treatment of non-monatomic materials at a fundamental level. At present in the QSCF and TFD models only monatomic materials' equations-of-state are calculated and a mixing scheme [11] based on adjustment of component densities to achieve the same mean pressure is employed to treat non-monatomic materials. This scheme is unable, except perhaps in an empirical sense, to describe the chemical binding which exists in the cold and warm materials.

II. Theory and results

We solve the time-dependent Schroedinger equation (expressed in atomic units) for orbitals of a given symmetry. For example for an atom we solve for orbitals of s, p_x, p_y, p_z symmetries, where the excited states of each symmetry are generated in the temporal solution [12]. Problems which take advantage of spherical symmetry, where available, by projection of radial Schroedinger

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equations, which is possible when the angular solutions are the set of spherical harmonics [1-3], require less numerical work in that one would solve one radial equation for all magnetic sub-orbitals (p_x, p_y, p_z for example); however we have gained the generality of being able to treat a potential of low symmetry within an ion sphere.

For the jth orbital for example we have the Schroedinger equation,

$$i \frac{\partial \chi_j(\vec{r},t)}{\partial t} = [-\frac{1}{2}\nabla^2 + V(\vec{r},t)]\chi_j(\vec{r},t) \quad .$$

(1)

The potential is given by the ansatz,

$$V(\vec{r},t) = -\Sigma \frac{Z_k}{|\vec{r} - \vec{r_k}|} + \int d\vec{r}' \frac{\rho(\vec{r}',t)}{|\vec{r} - \vec{r}'|} - (3\rho(\vec{r},t)/\pi)^{\frac{1}{3}}$$

(2a)

$$\rho(\vec{r},t) = \Sigma n_j |\chi_j(\vec{r},t)|^2 (e^{\frac{\epsilon_j(t)}{kT}} + 1)^{-1} \quad ,$$

(2b)

where the occupation number n_j is either 1 or 2, $\epsilon_j(t)$ is the quantum mean of the Hamiltonian in Eq. (1), and the summations over k and j run over the positions of the point nuclei and over the electronic orbitals respectively. Eq. (1) is solved starting at t = 0 with a linear combitation of Slater-type orbitals centered at

the nuclear positions.

We use of an algorithm (Fast-Fourier-Transform) in which the Laplacian is evaluated in transform rather than in real space. This allows us to find the solution at the boundaries of the grid box in apparent absence of physically spurious numerical reflections or other artifacts there. Futhermore the natural periodicity of the FFT algorithm implies that the grid box, in which the ion sphere is contained, is concatenated virtually in all three spatial dimensions. We believe that this virtual lattice is a sensible representation of the periodicity of the electronic density which is implicit in the ion-sphere model.

Numerical experiments have shown us that a stationary solution is obtained at $t \approx 10$ a. u. . Fig.1 shows the spectrom [12] at t = 10 a. u. for a temperature of 0.026 eV and density of 0.08 g/cc. As described in [12], knowing the eigenenergies from the spectral peak positions the eigenfunctions are calculated from another integration in which the eigenfunctions are the temporal Fourier transforms at the appropriate eigenenergies. The widths of the spectral peaks depend on the length of the temporal interval

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(10 a.u.); it is satisfactory to choose a t_{max} which resolves all peaks and for which stationarity of the mean Hamiltonian is achieved.

Fig. 2 shows the first two even-parity eigenfunctions for LiD corresponding to the first two eigenenergies of Fig. 1. The Li nucleus is centered at z = -1.5 a. u. and the D nucleus at z = 1.5 a. u. The eigenfunction with eigenenergy centered near -3.5 a. u. (Fig. 1) is nearly completely centered about the Li nucleus; the eigenfunction with eigenenergy centered near -1.0 a. u. (Fig. 1) is shared covalently between the two nuclei and thus its squared modulus or electronic density represents a sigma-type chemical bond in which the electronic density forms a cylinder along the bond.

In this calculation the time step is dt = 0.05 a. u. and a spatial grid in cartesian coordinates of dimension 32x32x32 is used. The volume of the ion sphere is calculated from the reciprocal of the material number density. We choose the length of an edge of our square computational grid box to be equal to twice the radius of the ion sphere. For mixed materials such as LiD the volume of the ion

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sphere is calculated from the reciprocal of the number density of the diatomic material (where the isotopic number for Li is 6), and the ion sphere radius is measured from the molecular midpoint. The internuclear axis is taken along the z axis. In the highly shocked material the length of the z-edge of the computational grid box is constrained to be larger than twice a bond length; otherwise the nuclei would eventually approach the box boundaries, invalidating the calculation. This constraint has a physical basis however, namely that a molecule is not very compressible along its bond. In these cases the grid box is taken to be a rectangle, instead of a square, with length of the x-edge and y-edge taken to be twice the radius of the base of the cylinder, with height along z equal to twice the bond length, whose volume is calculated from the reciprocal of the number density compressed diatomic material.

The parameters of the starting orbitals are sensibly chosen to minimize the energy. The spectrum and stationary energy tend to be insensitive to a range of variations about these values. Outside of this range however values exist which dramatically change the

spectrum; the new spectrum appears to correspond to an excited configuration. We use only the ground configuration. Electrons are thermally promoted from ground configuration orbitals into continuum orbitals.

Continuum states are calculated using the same numerical procedures as described above, except that the starting orbitals are taken to be plane waves with a known momentum and energy [10]. Solution of the time-dependent Schroedinger equation then evolves these orbitals into steady free-electron orbitals in the presence of a given potential. The use of plane-wave starting orbitals and a forward time integration insures that the evolved, steady orbitals satisfy outgoing boundary conditions [10]. A number of orbitals sufficient to span the continuum for a given temperature are used. The results are sensitive for a given temperature to having continuum orbitals available for occupation by thermally promoted electrons; we have therefore distrubuted the continuum energies from a value close to zero to eight times kT. If the range of energies are too narrowly distributed about kT, then we observe Fermi collapse, in which the material is not energetic enough for a

given temperature. This is a problem, characteristic of the quantum models [7], which TFD theory avoids by having the electronic density written analytically as an integral over electronic energies from zero to infinity. It is more important to span a wide swath of energy space for a given kT than it is, for a smooth continuum in absence of resonances, to take a fine grid in the integration over continuum energies. Here we find that use of nine continuum orbitals gives satisfactory results.

Knowing the bound eigenfunctions from the spectral calculation and the continuum orbitals from the procedure described previously, the electronic density is normalized to ensure electrical neutrality within the grid domain, which contains the ion sphere, by requiring that the volume integral of the density is equal to the number of electrons,

$$\int d\vec{r} \, \rho(\vec{r}) = Z \tag{3a}$$

$$\rho(\vec{r}) = \rho(\vec{r})_b + \rho(\vec{r})_c \tag{3b}$$

$$\rho(\vec{r})_b = \Sigma \, n_j \, | \chi_j(\vec{r}) |^2 \, (e^{\frac{\epsilon_j - \mu}{kT}} + 1)^{-1} \tag{3c}$$

$$\rho(\vec{r})_c = \frac{(2m/\hbar^2)^{\frac{3}{2}}}{4\pi^2} \int_0^\infty d\epsilon \, \sqrt{\epsilon} \, n_j \, | \chi_\epsilon^{(+)}(\vec{r}) |^2 \, (e^{\frac{\epsilon - \mu}{kT}} + 1)^{-1} \quad , \tag{3d}$$

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where μ is the chemical potential, which is adjusted such that Eq. (3a) is satisfied.

The pressure is calculated from the virial theorem, using the difference of the mean kinetic energy and the virial of Clausius rather than the surface integral [13]. The energy is calculated from the mean of the many-electron Hamiltonian. In both cases the variationally-derived Kohn-Sham exchange contributions are included [13-14].

We show comparisons of the shock Hugoniot for LiD for the present and the INFERNO models, where the materials mixing scheme described by More et al. [11] has been used in the INFERNO calculation. The Hugoniots are calculated by solving the Rankine-Hugoniot equation by interpolation on tables of pressure and energy isotherms. The initial density of 0.823 g/cc is close to normal and was chosen to give an interpolated Hugoniot with the least amount of numerical noise. Some amount of numerical noise in the isotherms seems hard to avoid in quantum calculations due to the difficulty of converging the calculation to self-consistency at every temperature-density point. The agreement is reasonably good

considering the differences between the two models. The present model gives a slightly more compressible Hugoniot, which would seem to be consistent with the increase in phase space available to electrons moving in the field of two nuclei per unit of material in comparison to that available to electrons moving in the field of one nucleus per unit of material [11].

In conclusion we have developed a finite-temperature spectral theory of materials' equation-of-state. The method generates a spectrum of electronic states in a single temporal integration pass. Knowing the spectrum the eigenfunctions can be recovered in a second integration pass and used to calculate the electronic pressure and energy of the material.

The use of a 3D Schroedinger-equation solver allows us to treat chemically mixed materials at a fundamental level. The use of the FFT solver automatically posits periodic boundary conditions for the computational grid box; this is consistent with the naturally occuring periodicity of condensed materials and eliminates the ion-sphere boundary uncertainty of QSCF models [1-3].

Finally the authors of [3] conclude that their QSCF results

suggest "that our understanding of dense, partially ionized matter is good," to which I reply, with Hardy [15],

> That I could think there trembled through
> Their happy good-night air
> Some blessed hope, whereof they knew
> And I was unaware.

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Figure Captions

Fig. 1. Spectrum of LiD at T = 0.26 eV and ρ = 0.08 g/cc.

Fig. 2. Eigenfunctions versus z corresponding to the two spectral peaks given in Fig. 1. The Li nucleus is centered at z = -1.5 a. u. and the D nucleus is centered at z = 1.5 a. u.

Fig. 3. Shock Hugoniots for LiD. The initial temperature is 0 .026 eV and the initial density is 0.823 g/cc. Heavy curve: INFERNO model with mixing scheme of Ref. 11; light curve: present model.

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